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Techno-productive potential of photosynthetic microbial fuel cells through different configurations

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ABSTRACT

The shortage of sustainable energy and the extensive environmental pollution along with the global warming effect caused by CO_2 emissions are major problems facing the world today. The use of microalgae to overcome these problems has gained enormous research interests in recent years, primarily due to their ability to convert CO_2 by photosynthesis into potential biomass. The merging of such phototrophic organisms into microbial fuel cells (MFCs) is an interesting option since they can act as efficient in situ oxygenators, thus facilitating the cathodic reaction of photosynthetic microbial fuel cells (PMFCs). Also, microalgae can support the efficient removal of phosphorus and nitrogen, as the MFC technology cannot stand-up alone in this field. But such PMFC configurations does possess several challenges, among which PMFC design, output current and sustainability are the major bottlenecks encountering large scale implementation for electricity generation in a cost-effective way. This review goes beyond previous research work by providing not only a detailed update on the current PMFC configurations, but also the critical operational parameters of PMFC, with a scope that extends to cover all types of direct or indirect integration of phototrophic microbes within MFC technology.

Contents

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Nomenclature

MFC	microbial fuel cells
PEM	proton exchange membrane
DO	dissolved oxygen
COD	chemical oxygen demand
PAR	photosynthetically active radiation
BESs	bioelectrochemical systems
PMFCs	photosynthetic MFCs
PBR	photobioreactor
PhFC	photo-biological fuel cell
PSMFC	photosynthetic sediment MFC
SMFC	sediment microbial fuel cell
MCC	microbial carbon capture cell
MSC	microbial solar cell
PCE	power conversion efficiency
HRT	hydraulic retention time

1. General concepts

1.1. Microbial fuel cells technology

Microbial fuel cells (MFCs) are one of the rapidly evolving technologies for bioelectricity generation [1–6]. Typical MFC, illustrated in Fig. 1, contains two chambers, anodic and cathodic, separated by a proton exchange membrane (PEM) [7]. Throughout this technology, microorganisms can metabolize organic substrate in the anodic chamber to produce electrons and protons, in which the electrons are shifted to the surface of the anode, afterwards flowing to the cathode through an external circuit, while the protons migrate to the cathode through PEM [1,3,4,8,9]. Both electrons and protons are combined with the reduction of oxygen to water in the cathode chamber [10–15].

There are multi in/outflow gases through the different compartments of MFC [16,17]. The concentration of inflow oxygen in cathode chamber affects greatly the power output of the MFC. The effect of dissolved oxygen (DO) concentration in the cathode chamber on the power production performance of MFC was studied, [11,18] and it was concluded that the optimum DO concentration is around 6.6 mg/l. This proves the oxygen limitation of MFC current generation when DO concentration in the cathode chamber is less than 6.6 mg/l. Normally, oxygen in the cathodic chamber is provided by atmospheric air for a single cell MFC, with the cathode directly exposed to air, or by mechanical aeration for a dual-cell MFC. CO_2 is the outflow gas verified as the main gaseous end product when either glucose, acetate or real wastewater is used as a substrate [19]. The alkaline condition in cathode chamber increases the possible absorption of CO_2 from the anode. This condition develops due to the accumulation of hydroxide ions (OH^-) which results from the cathode oxygen reduction [11,20]. Oxygen gas delivery and CO_2 gas accumulation remain among the major limiting factors in the practical application of MFC, which could be overcome by looking for efficient, inexpensive, non-toxic and sustainable catalysts for the cathodic reaction [21].

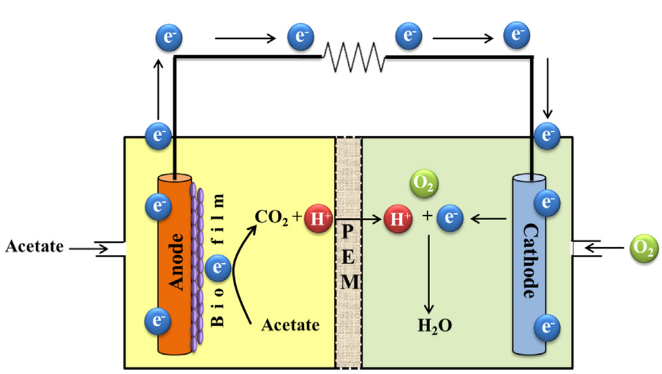

Fig. 1. Schematic diagram of a classic microbial fuel cell with anaerobic anode chamber and aerobic cathode chamber separated by a proton exchange membrane (PEM).

1.2. The power of microalgae

Algae convert solar energy into several forms of biochemical energy in which they account for more than half of the primary photosynthetic throughput on Earth [22–25]. The concern for microalgae is growing globally due to their high growth and CO_2 fixation rates which could reach up to 6.24 kg/m^3/day and this reflects the great opportunities contained by the solar energy conversion via photosynthetic microorganisms [26,27]. The photosynthesis process could be considered as one of the complex biological redox reactions that is naturally carried out by algae and plants, in which they are able to harvest the solar energy to produce carbohydrates and oxygen through multiple redox reactions, as well as producing additional compounds, which may be utilized for energy or employed in the synthesis of other molecules as illustrated in Fig. 2 [28,29].

Autotrophic growth is the most common technique for microalgae cultivation, in which they are cultivated in natural or artificial illuminated environments. Under this condition, the cells use CO_2 as a carbon source and capture light energy. Few microalgal species can use the feasible alternative of heterotrophic growth capacity in the absence of light instead of photosynthetic regime in photobioreactors (PBR; see Box 1), by substituting the atmospheric CO_2 fixation with available organic carbon sources in the culture media. Autotrophic and heterotrophic modes could be combined in mixotrophic growth mode, in which photosynthetic and respiratory metabolism operates in parallel with simultaneous

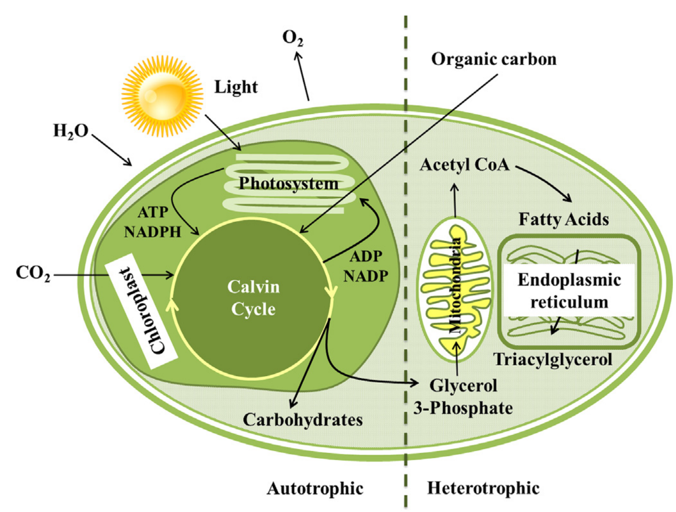

Fig. 2. Schematic representation of autotrophic (photosynthesis and CO_2 fixation) and heterotrophic (organic carbon) metabolism in microalgae cells; with only the major steps. Pathways are detailed in references [100,101].

Box 1–Explanation of terms.

Photobioreactor (PBR)
A bioreactor that incorporates light source to provide photonic energy input to photosynthetic microorganisms in which photofermentation takes place [96].

Upflow MFC
A simple scalable structure of MFC working in continuous upflow mode and omits ion exchange membrane [73].

Photosynthetic microbial fuel cell (PMFC)
A bioelectrochemical system capable of converting sunlight into electricity based on the exploitation of biocatalytic reactions within active microbial cells [46].

Photo-biological fuel cell (PhFC)
A device where photosynthetic organisms act as a biocatalyst to transform light energy to bioelectricity by utilizing CO_2 or organic sources as substrates [75].

Biocathode
Employs use of microorganism capable of utilizing cathode terminal as electron source [97].

Microbial solar cell (MSC)
Specialized reactors used for light/ electricity conversion by applying microbial phototrophs [74].

Photovoltaics
Devices that convert light into electricity [74].

Lagooning technique
The accumulation of wastewater in ponds or basins, where a synergistic effect of heterotrophic microorganisms and algae occur. Algae produce oxygen, while heterotrophic microorganisms deplete organic matter using oxygen [79].

Microbial carbon capture cell (MCC)
A new sustainable form of MFCs with the capability of converting the generated carbon dioxide from organic wastewater treatment to useful biomass with photosynthetic microorganism [42].

assimilation of CO_2 and organic carbon, respectively [30,31]. The heterotrophic growth mode overcomes the major shortage of illuminated autotrophic PBR by practically allowing the use of any bioreactor without the need for special design or equipment. Some algal strains under heterotrophic mode can have a high dry biomass, growth rate, ATP production and yield, *N* content and lipid content, compared to autotrophic mode [32–37]. On the other side, heterotrophic cultures have several key restrictions, in which there are a limited number of heterotrophic microalgal species. Also, energy expenses increase by supplementing an organic substrate with the chance of growth inhibition by surplus organic substrate and failure to produce light-induced metabolites. Moreover, this mode of cultivation is subjected to contamination and competition with other microorganisms [38].

2. Integrating microalgae and MFC

Photosynthetic organisms recruit charge separation and discharge electrons and protons, during flow chain reactions, so it is possible to capture energy in the form of bioelectricity using photosynthetic metabolism in the MFC system. This process is mimicking the lagooning technique (see Box 1) which is a commonly used natural treatment process. The synergistic effects between heterotrophic microorganisms and algae are taking place during this treatment, in which oxygen is produced by algae using solar energy and metabolizing nutrients and bicarbonates produced by heterotrophic microorganisms metabolizing organic matter and oxygen. Through this integration, the traditional aeration systems could be replaced by the more environmental and economic sustainable photosynthetic one [39]. Thus, it is assumed that electricity can be produced by the growing cathodic algae in MFC, where oxygen is produced by the photosynthesis process [40].

This assumption has been applied in MFC by the utilizing of a substrate which is oxidized at the anode and employing an algal biocathode (Box 1) which act as a biological electron acceptor and concurrently reducing CO_2 to biomass. Normally in these configurations, a mediator is used in the cathode chamber for electrons shuttling. The electrons flowing from the anode side are transferred into the catholyte and reduce the oxidized state mediator, which then penetrates the algal cells to release their electrons load and become oxidized again. The growing algal cells consume these shuttled electrons in their metabolic pathways to transform CO_2 into oxygen and biomass. The cells release the oxidized mediator to the media and the cycle is repeated where the mediator is once again reduced by the electrons in the catholyte [41]. The general biochemical reactions, during illumination, that take place at the anode and cathode are exemplified by Eqs. (1) and (2), respectively [42].

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

$$6CO_2 + 12H^+ + 12e^- \rightarrow -C_6H_{12}O_6\text{-(biomass)} + 3O_2 \quad (2)$$

Algae carry out photosynthesis when they are illuminated, using CO_2 and light to produce organic matter and biomass, while they consume oxygen during dark and oxidize the formerly produced organic matter to get energy (Eq. (3)) [43].

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad (3)$$

On the other hand, some photosynthetic cyanobacteria, i.e. *Spirulina platensis* could be used as a bioanode catalyst, where the electrochemical potential is maintained by the formation of biofilm that can accept the generated electrons directly without the need of mediator [44–46].

3. Obstacles of photosynthetic MFC

Microalgal cathode-assisted MFC is falling under biocathodes category, which is attracting growing attention due to their advantages compared to abiotic cathodes, i.e. sustainable process and inferior costs [47]. Although microalgae can provide the advantages of high cell density with high reaction velocity and resistance to hazardous materials through a flexible and stable operation, [48,49] but effective CO_2 supply becomes a problematic aspect in the case of microalgal MFC with high-density biomass [50]. Generally, MFCs with biocathodes are in need of further improvement as great overpotentials are expressed, which result in some energy loss [51,52]. Also, resistance of charge transfer is quite a problem accompanied with open air biocathodes, even though the oxygen mass transfer restriction is reduced [53].

Power generation is affected by the thickness of cathodic biofilm in a different manner, where it was observed to steadily decline with the growth in cathode biofilm thickness on both of electrode and current collector [54]. Also, shortening the startup time for biocathodes is challenging the effective application of this technology [53]. Regarding the biocathodic microorganisms, alteration in pH can modify the surface features of the cells within the biofilm including net electrostatic charge, hydrophobicity, cell morphology and size along with biofilm structure, all of which can disturb the biocatalytic activity [55,56]. Despite the necessity of using a buffer system to control pH in bioanode and biocathode, it has turned out to be one of the challenges for MFCs with biocathode, since sustainable MFCs have to operate at high rates with the minimal dependency on chemicals usage. The role of carbon source is another important concern, in which carbon-limited conditions in

biocathode affect its performance. Autotrophic biocathodes have been used widely in aerobic and anaerobic biocathode MFCs, where the sole carbon source for microorganism growth is the inorganic carbon, [53,57–61] in which several implications exist in terms of MFC operation and startup time, due to the slower nature of autotrophic growth compared to heterotrophic one.

Moreover, the molecular diffusion and electro-osmosis are challenges towards the high performance of biocathode MFCs, occurring due to the crossover of organic materials from the anode to the cathode side through the separating membrane. This crossover can reduce cathode potential and alter its surface structure leading to a potential toxicity to its catalytic agent, which adversely disturbs system performance and Coulombic efficiency [62–67]. Also, the high chemical oxygen demand (COD) content inflowing to the biocathode can allow the growth of aerobic heterotrophs, in which the cathode will be turned irreversibly into an aerobic heterotrophic biofilm and consequently oxygen supply is restricted to the cathodic biofilm inhibiting electricity production [54,68].

On the other side, microalgae grow in bioreactors or open ponds where they exploit photosynthesis using sunlight, CO_2 and other nutrients to grow and reproduce, which highlights the urgent need of new MFC designs in order to adjust the supply of light, CO_2, and nutrients to the microalgae. The core of these new constructions is attributed mainly to illumination due to its direct effect on the high biomass yield of many algal species which is constrained by the laws of thermodynamics illustrating that maximum photosynthetic efficiency could be achieved by using eight photons of photosynthetic active radiation (PAR) to convert one molecule of CO_2 into carbohydrate [69]. Overall, biologically catalyzed cathodes generate low power compared to the chemically catalyzed ones, which is considered as the main challenge facing microalgal cathodes in the short term.

4. Configurations of photosynthetic MFC

Solar energy technologies are gaining increasing concern due to the growing attention about sustainable energy resources. Innovative methodologies to convert solar energy into bioelectricity developed with bioelectrochemical systems (BESs) in the last ten years, in which many of these photovoltaic devices (Box 1) have the ability to separate photosynthetic energy and heterotrophic dark electricity production in the absence of artificial mediators. Photosynthetic MFCs (PMFCs; see Box 1) are the one which employ an anode or cathode, with a biofilm enclosing photosynthetic microorganism, in which photosynthesis is carried out and as a result they act as electron donors and also as producers of organic metabolites. Also, removal of carbon dioxide by this integrated PMFC is another additional benefit [61,70]. Configuration of such PMFCs is the main challenge in order to increase the power density and obtain long-term performance so as to get a cost-effective system. Four different configurations of PMFCs are schematized and detailed in the following sections.

4.1. Coupled PMFC

In this integrated type of PMFC, half or full bioanodic MFC is connected to a PBR, in which CO_2 is pumped directly from the MFC to the PBR. This configuration operates in the absence of ion exchange membrane which simplifies its structure and makes it cost-effective to scale up.

A photosynthetic microbial cathodic half-cell, using the *Chlorella vulgaris* microalgae as the direct electron acceptor, was developed earlier, [41,71] in which the half-cell is integrated to a fermentative yeast anode, creating a complete coupled MFC (Fig. 3A). This design was tested into an existing bioethanol plant to create coupled MFC with the existing industrial yeast bioreactor acting as anodic half cells. This dual benefit integrated system is used to generate power for the existing bioethanol plant, and simultaneously metabolize CO_2 emissions, from bioethanol production, through photosynthesis by the microalgae growth in the cathodic PBR half-cell. Moreover, the biodiesel is produced as an energy byproduct during the growth of microalgae. For all of these benefits to be obtained, a chemical mediator must be added to the anodic half-cell to allow electrons shuttling between yeast cells and the electrode. The cathodic half-cell was aerated with feed-air containing 10% CO_2 which is sparged directly into the cell culture, and illuminated by sunlight to facilitate photosynthesis process by microalgae in the PBR.

The same concept was modified by connecting a glass PBR to MFC to form the PMFC [72]. The illuminated PBR was used for the initial startup of algal growth with air pumped inside the reactor via a sparger, while the MFC has dual electrodes separated by a cation exchange membrane. The growing microalgae are photosynthesizing and converting light energy to chemical energy in the form of biomass, in which electricity is produced with

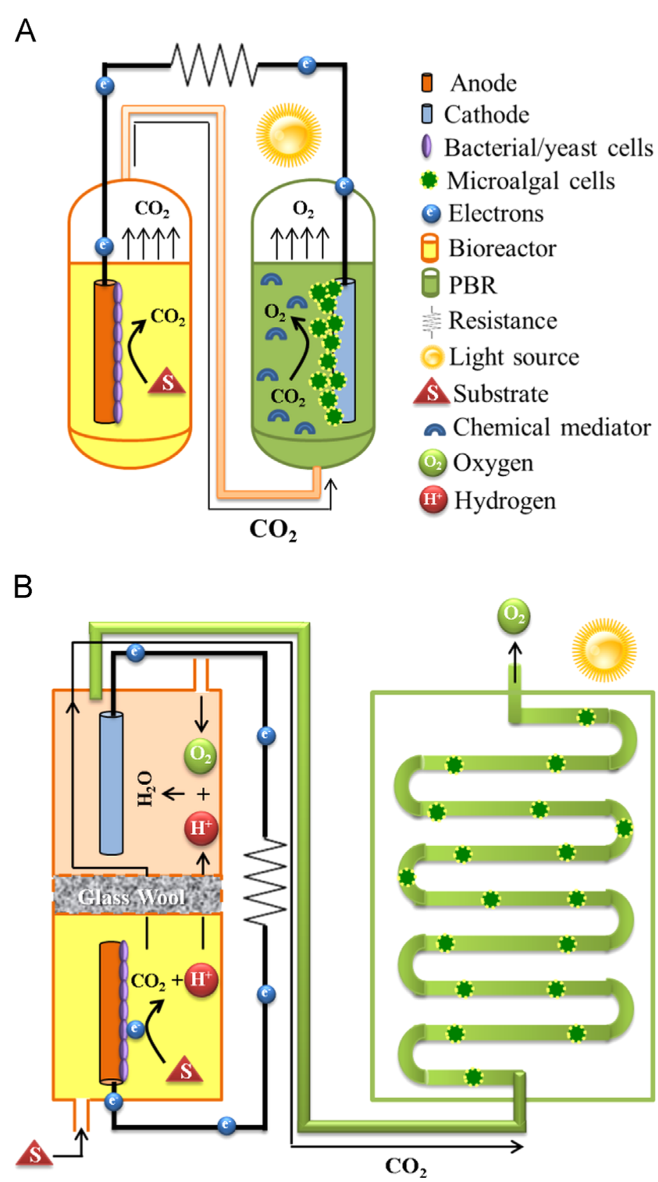

Fig. 3. Schematic configuration of coupled PMFC; (A) PBR based design and (B) upflow MFC based design.

electrochemically active bacteria in the anode compartment of the MFC. Also, a similar design was proposed by Jiang et al., [73] in which upflow MFC (Box 1) and PBR coupled system for bioelectricity generation and wastewater treatment was developed (Fig. 3B). The upflow MFC mainly consisted of a plastic cylinder with carbon fiber brush electrodes, and glass wool/bead layers separator between anode and cathode compartments. An external column PBR was coupled with the upflow MFC, in which the effluent from the cathode compartment of the upflow MFC was continuously pumped into the column PBR. The microalgal culture was grown under continuous illumination and a purge of CO_2 (effluent of MFC) and air mixture gas.

4.2. Single chamber PMFC

The ability of some photosynthetic microbes, i.e. *S. platensis* to directly shuttle electrons to the electrode, without the need for mediators, was employed in a membrane-less single chamber PMFC design with photosynthetic bioanode. This design was proposed by several workers, [44–46] in which a simple scheme that allows the direct attachment of microalgae to the anode was suggested to construct an electrical power generator (Fig. 4A). Some blue–green microalgae were employed as a biocatalyst for electricity production. The anodic microalgal biofilm can create the required electro-potential, where the respiration reaction in the dark and the photosynthetic reaction in light can generate current. This configuration includes anode and cathode electrodes in a single chamber without a separating membrane.

In order to improve the efficiency of the single chamber PMFC, mixed culture of bacterial and microalgal cells was introduced in a synergistic approach, [74] in which the microalgal cells have the capability of producing organic materials, i.e. acetate, which are assimilated by the bacterial cells as a substrate for electricity generation (Fig. 4B). This design can be used as a general MFC and portable bio-battery, with the main application of electrical power production in both light and dark conditions as the photosynthetic reaction activated by illumination is considered as a reversible process for recharging the MFC to operate for long time.

Photo-biological fuel cell (PhFC; Box 1) is another type of the single chamber PMFC, [75,76] in which a PEM is sandwiched between anode and cathode. Microalgae were used to form anodic biofilm with atmospheric CO_2 as a carbon source in mixotrophic nutritional mode, which increases the feasibility of the association between autotrophic and heterotrophic metabolism in the same system by facilitating the conditions in which all types of CO_2 (atmospheric and organic) could be consumed.

4.3. Dual chambers PMFC

The dual chamber PMFC is considered the most common design that uses the algal photosynthesis as the source of oxygen in the cathodic chamber of PMFC [40,42,77–82]. This setup is consisting of a PMFC with two chambers separated by a PEM. Normally, activated sludge from a wastewater treatment plant is used as the inoculum for the anodic compartment which is covered during operation to exclude light and thus to avoid the appearance of algae, [79] whereas, the cathode compartment contains a culture of microalgae, which is illuminated for 12 h a day. The CO_2 produced by the anodophilic bacteria is transferred to the cathode compartment in some of these configurations in order to be utilized by the microalgae through the photosynthesis process. This could be applicable through introducing a vent at the top of each chamber which is connected by a tube with a funnel shaped gas collector placed in the anode side in order to facilitate the piping of the produced CO_2 into the cathode for microalgal biomass production via photosynthesis (Fig. 5).

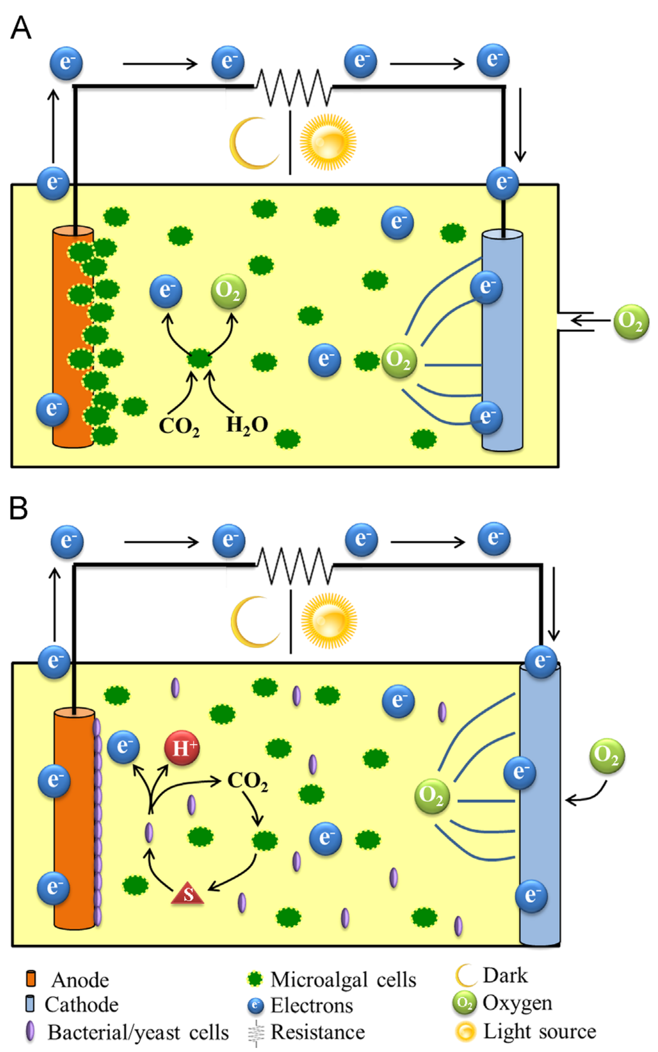

Fig. 4. Schematic configuration of single chamber PMFC; (A) microalgae catalysed design and (B) co-culture (bacteria and microalgae cells) catalysed design. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

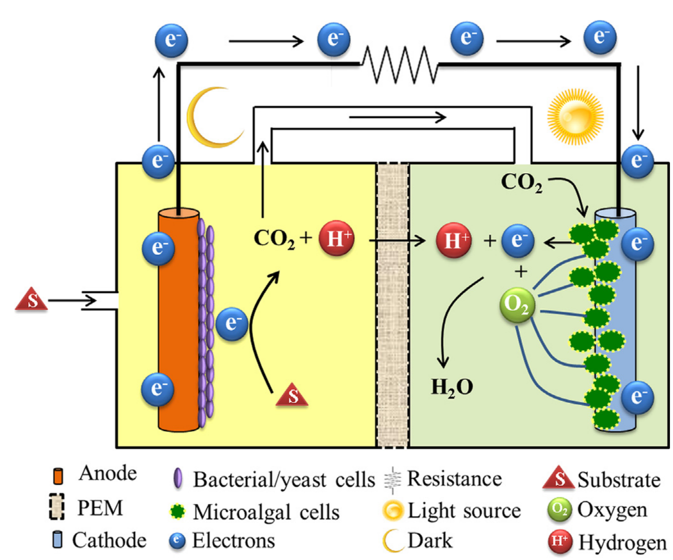

Fig. 5. Schematic configuration of dual chambers PMFC.

Alternatively, microalgae could be employed as a bioanodic catalyst within a dual chamber PMFC separated by PEM with a chemical cathodic catalyst [83,84]. Overall, the dual chamber setup can be efficiently started up by a forthright three-stage process entailing the separate production of bacteria and microalgae cultures followed by the substitution of the mechanical aeration system by the microalgae culture and finally a shift in the light dosage from the continuous input to the dynamic light/dark regime.

4.4. Photosynthetic sediment MFC (PSMFC)

The generation of energy could be achieved through the naturally existing differences in electro-potential, [85] by using an anode which is buried in sediment and a cathode immersed in the water laying on top of the sediment. Such configuration is called sediment microbial fuel cell (SMFC) or benthic MFC [86]. This energy is obtained through the reducing power of micro-organisms in the sediment, directly created by the oxidation of organic molecules or the redox reactions of inorganic reduced complexes, i.e. sulphur, while the cathodic reaction of the SMFC includes the reduction of electron acceptors like the dissolved oxygen in water.

A new construction which incorporates microalgae in SMFC was proposed, in which cathode compartment was switched to biogenic one [50]. The CO_2 produced by anodic bacterial activity is consumed by algal cells, and the O_2 produced by the algae is consumed by the PSMFC cathode compartment for current production. This PSMFC is generally consisting of an anode placed in the middle of a sediment layer which is covered with sand and a cathode compartment which is filled with microalgal culture medium. The PSMFC is normally operated in the presence of a light source in order for the photosynthesis to take place (Fig. 6).

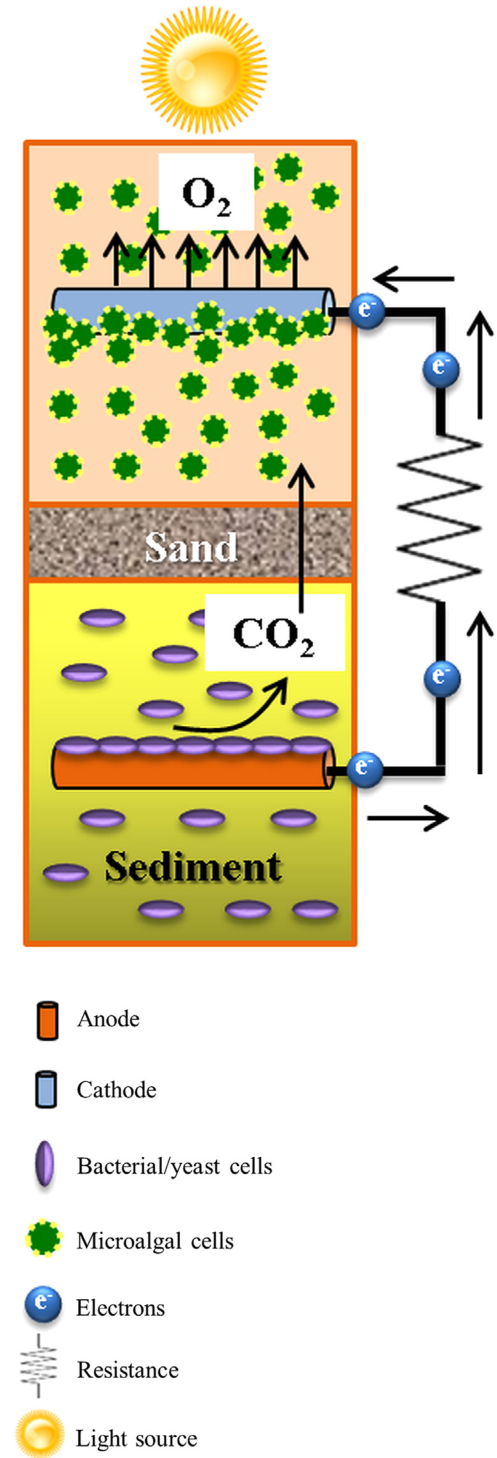

Fig. 6. Schematic configuration of photosynthetic sediment MFC (PSMFC).

5. Power generation by PMFC

Generally, microalgae could be cultivated in the anode or cathode compartments of the PMFC. Anodic microalgae are used directly to generate current due to its ability to assimilate substrate producing electrons and transferring these electrons directly to the anode without the aid of a shuttling mediator. The role of cathodic microalgae is different, where they are used as biological oxygenators instead of the mechanical ones which add up to the total cost of generated energy of MFC. Several trials were investigated (Table 1) in order to obtain the maximum benefits of microalgal MFCs either in anode or cathode compartments.

5.1. PMFC with anode catalyzed microalgae

Microalgae are generally cultivated in the anode side of the PMFC in order to develop a biofilm which has the ability to assimilate a substrate generating electrons, which are then delivered to the anode either directly or via a mediator [87]. *S. platensis* is one of the microalgal species that has the ability to shuttle electrons directly to the anode without the need of mediator, and based on this ability, it was investigated by several authors for current generation using a single chamber membrane-less and mediator-free PMFC [44–46]. Different electrode types were employed in these studies, i.e., gold [46] and platinum [44–46]. The power density obtained out by Fu et al. [45] was 1.64 mW/m^2, which was amplified by Lin et al. [46] to reach 10 mW/m^2, probably due to the usage of gold anode and graphite cathode. In this type of PMFC, *S. platensis* is carrying out the photosynthesis reaction to produce oxygen as a by-product while exposed to light, which then acts as an oxidant and possibly inhibits anodic oxidation reactions, reducing the generated electrical power [88]. Also, it was shown that the chlorophyll content of the microalgal biofilm affected the PMFC's electricity generation, where lower voltage is obtained in light conditions compared to dark conditions, which could be due to a discharging manner. This negative impact of light on the voltage is reversed with other PMFC configurations in which light intensity increases the output voltage [89–91].

The same PMFC configuration, but with membrane included, was operated with mixed culture of microalgae inoculated in the anode side, [75,76] in order to achieve a sustainable system which

Table 1
Outline of the main characteristics of PMFC setups and their generated current.

General design	Anodic biocatalyst	Anode material	Anolyte	Cathodic biocatalyst	Cathode material	Catholyte	PEM	Illumination system	Current density (mA/m^2)	Power density (mW/m^2)	Reference
Single chamber	*S.*[a] *platensis*	Gold	Zarrouk medium	–	Graphite	Zarrouk medium	–	D	168	10	[46]
	S. platensis	Pt[b]	Buffer medium	–	Pt	Buffer medium	–	L	45	6.5	[44]
	S. platensis	Pt	Zarrouk medium	–	Pt	Zarrouk medium	–	D	0.8	1.64	[45]
	Mixed microalgae	Graphite	Wastewater	–	Graphite	Air	Nafion	L/D[c]	0.25	0.004	[76]
	Mixed microalgae	Graphite	Acetate	–	Graphite	Air	Nafion	L/D	19	76	[75]
	G.[d] *sulfurreducens*	Graphite	Acetate	*Ch. reinhardtii*	Pt	Air	–	D	120	41	[74]
Dual chamber	Activated sludge	Graphite	Synthetic wastewater	*C.*[e] & *Phormidium*	Graphite	Minerals	Nafion	L	10	3.35	[40]
	–	Graphite	Potassium ferrocyanide	*C. vulgaris*	Graphite	Bolds basic media	Salt bridge	L	–	2.7	[41]
	Mixed bacteria	Carbon cloth	Synthetic wastewater	Mixed microalgae	Carbon cloth	Lagooning wastewater	Sterion	L/D	129.8	12.6	[79]
	Activated sludge	Carbon cloth	Fruit processing waste	*C. vulgaris*	Carbon cloth	Bold's basal medium	Sterion	L/D	117	14.4	[43]
	Activated sludge	Carbon fiber	Acetate	Mixed microalgae	Carbon fiber	Pond water	CEM[f]	L/D	11	7	[78]
	Activated sludge	Carbon felt	Glucose	*C. vulgaris*	Carbon fiber	BG11 culture medium	CEM	L/D	8 (A/m^3)	2.5 (W/m^3)	[42]
	Domestic wastewater	Carbon fiber	Glucose	*C. vulgaris*	Carbon cloth	BG11 culture medium	CEM	L	11 (A/m^3)	5.6 (W/m^3)	[80]
	Ch.[g] *reinhardtii*	Graphite	TAP[h] medium	–	Graphite	Potassium hexacynoferrate	Nafion	L	–	13	[82]
	Ch. reinhardtii	Graphite	TAP medium	–	Graphite	Potassium hexacynoferrate	Nafion	L/D	–	0.82	[81]
Coupled	Activated sludge	Carbon fiber brush	Wastewater	–	Carbon fiber brush	Anodic effluent	–	L/D	1.3 (A/m^3)	0.5 (W/m^3)	[73]
	Mixed bacteria	Graphite	Acetate	–	Graphite	Potassium hexacynoferrate	CEM	L/D	539	110	[72]
PSMFC	Sediment	Graphite	Glucose	*C. vulgaris*	Graphite	Bold's basal medium	–	L	48.5	–	[50]

[a] S.: *Spirulina*.
[d] G.: *Geobacter*.
[g] Ch.: Chlamydomonas.
[b] Pt: Platinum.
[h] TAP: Tris acetate phosphate.
[e] C.: *Chlorella*.
[f] CEM: Cation exchange membrane.
[c] L/D: 12 h light/12 h dark.

is able to strive on CO_2 and simultaneously obtain a value added biomass in a biorefinery concept. Low power density was obtained (0.004 mW/m^2), probably due to the presence of different strains in the mixed culture with different abilities toward direct electron shuttling to the anode. Also, the low power could be attributed to the mixotrophic mode that was applied using both the atmospheric CO_2 and wastewater as carbon sources. Dissolved oxygen produced during the photosynthesis process was found to be the major restrictive factor toward dropping performance. On the other side, electrons installed at the electrode in light condition were higher compared to that installed in dark condition under oxygenic environment [75].

The effect of light on the PMFC power density was further studied by Lan et al. [84] in terms of light source and intensity, as they can affect greatly the chlorophyll development, stomata opening and photosynthesis process in microalgal cells. In order to be confirmed, the *Chlamydomonas reinhardtii* was used as a bioanode catalyst in PMFC and was illuminated with monochromatic red and blue lights with different intensities. The obtained PMFC power density was directly proportional to light intensity, with the superiority of red light to blue one, with maximum value of 13 mW/m^2. The same microalgal strain was used in another study to optimize the electrode distance within two chambers PMFC with graphite electrodes and the application of dynamic light/dark regime [83]. Maximum power density of 0.82 mW/m^2 was achieved at electrode distance of 14.7 cm, with a significant reduction in the internal resistance.

5.2. PMFC with cathode catalyzed microalgae

Microalgae are commonly used as biocathodes in the PMFC in order to replace the conventional mechanical aeration methods which could be a more sustainable alternative in both economic and environmental terms [92]. Also, algae-assisted cathodes can cooperate in reducing the emitted CO_2 from bacterial metabolism and respiration. *C. vulgaris* is one of the most common microalgal species that was investigated by several authors as a biocathode in PMFC. One of the first trials was conducted by Powell et al. [41] to study the capture of CO_2 by *C. vulgaris* which acted as an electron acceptor in the cathode chamber of PMFC. The maximum cell growth rate (3.6 mg/l/h) was achieved under a concentration of 10% CO_2 with obtained power density of 2.7 mW/m^2. Algae assisted cathodes were further employed to produce low cost oxygen in order to transform MFC to a complete microbiological system. This trend was adopted through the construction of two chambers PMFC with included membrane and wastewater used as anolyte [43,80]. With the application of different illumination regimes to the cathode (12–24 h of light), the critical role of light in PMFCs was again confirmed by observing the decline in dissolved oxygen in dark mode with cell voltage following the same trend of dissolved oxygen profile, resulting in a power density of 13.5 mW/m^2 during the acclimation phase [43]. Additionally, reduction of CO_2 emission by *C. vulgaris* was targeted by Wang et al. [80] through the introduction of a new PMFC termed as microbial carbon capture cell (MCC; see Box 1). All the generated CO_2 from anode was completely removed by catholyte, while the soluble inorganic carbon was transformed into algal biomass. The output voltage of the MCC (610 mV) was comparable to that of the MFC (630 mV) with maximum power density of 5.6 W/m^3. This confirmed the ability of algae to generate the required oxygen for the PMFC system under optimum operating conditions, although the generation of electricity was not stable due to the fluctuation in dissolved oxygen concentration, which is illumination dependent factor. Also, it was discovered that the cathode polarization resistance is higher than that of the anode which means that the cathodic reactions are the restrictive element in this technology [80]. In order to decrease such resistance, *C. vulgaris* was immobilized and introduced as a biocathode in MCC to simultaneously treat wastewater, generate electricity and produce biodiesel [42]. Chemical oxygen demand (COD) removal of 85% was achieved with a maximum power density of 2485.35 mW/m^3. Compared to the suspended cells, Coulombic efficiency of immobilized ones was improved by 58%.

The improvement of PMFC was extended to the type of employed substrate, in which natural organic-rich sediment was used in the anode compartment of PSMFC in order to assess the applicability of *C. vulgaris* for PSMFC operation deprived of any external oxidant [50]. The increase in CO_2 production from the PSMFC was observed to be dependent on the generated current which in turn inhibits the production of CH_4. This reflects the capability of PSMFC to provide a method for producing microalgal biomass by CO_2 produced via the oxidation of organics based on current generation.

The effect of light intensity on the power production of PMFC was also inspected by using a microalgal co-culture of *Chlorella* and *Phormidium* [40]. Covered anodic PMFC exposed to lower power of light (6 and 12 W) exhibited higher Coulombic efficiency and power than the one with higher powers (18 and 26 W), which means that high light power should be avoided if algal photosynthesis is the source of oxygen in the cathodic chamber of PMFCs. This study drew the attention toward the benefits of using more than one strain of microalgae in PMFCs by employing water ponds containing mixed cultures of microalgae [77,78]. The first study was conducted with a mediator-less mixed microalgal cathodic PMFC to produce oxygen as a replacement for mechanical aerator [78]. The cell was started-up without the algal mixed culture, which was then added in order to replace the mechanical aeration, with the shift from continuous light exposure mode to light/dark mode. The cell voltage was comparable to that aerated mechanically, with the clear effect of organic load and illumination on electricity production. Similar results were obtained by Gajda et al. [77] illustrating the dependence of oxygen production by PMFC on light exposure which could increase power generation up till 42% after optimization. Moreover, the syntrophic interactions between electricity-generating bacteria and microalgal phototrophs were explored through an attempt to build a microbial solar cell (MSC; Box 1) using co-cultures of the *Ch. reinhardtii* microalgae and the iron-reducing *Geobacter sulfurreducens* bacterium [74]. The maximum power density was 41 mW/m^2 and the metabolite analyses showed that the *Ch. reinhardtii* produced formate in the absence of light, which was oxidized by *G. sulfurreducens* to generate current.

5.3. PMFC with integrated PBR

Microalgae could be incorporated in PMFC indirectly by connecting the MFC to a PBR, in which the generated gases are exchanged. This configuration was proposed by several researchers; Jiang et al. [72,73] developed a coupled system containing an upflow membrane-less MFC and a PBR in order to treat wastewater and generate electricity. The process started with feeding wastewater to the upflow MFC to reduce COD, phosphorus and nitrogen along with generation of electricity. The cathodic effluent was pumped to the PBR for removing the residual phosphorus and nitrogen via microalgae. The maximum power density obtained was 481 mW/m^3, and 78% of the COD was removed. The same configuration was proposed by Strik et al. [72] but with a membrane separating the two compartments of the MFC. The proposed PMFC produced electricity regularly for 100 days, with maximum power density that reaches 110 mW/m^2. This integrated configuration takes the advantage of the continuous treating of

domestic wastewater along with producing electricity and algal biomass.

6. Microbial versus non-microbial solar cells

The absence of any greenhouse gases emissions and the fast progress toward the feasibility and efficiency are the main advantages of photovoltaic solar panels, which represents the building block of any green energy technology. On the other side, solar panels suffer from limited long-term sustainability and difficulties in recycling their constituted materials, as well as, the intermittent of solar energy production due to the absence of sun light in night and winter, which highlight the importance of energy reservation technologies [93].

The use of biological materials could be the prospect alternative to the conventional solar cells in order to overcome these disadvantages. One of these biological options is the MSC, in which solar energy is captured by photo microorganisms through the photosynthesis process. The electrochemical analyses of MSC indicate that the catalytic activity of biocathode reduces over time if illumination is provided during growth, although it remains quite stable if growth occurs in the dark [94]. The biological materials are normally comprised of abundant elements, which are created by organisms merely as part of their regular metabolism. This reflects on the low stability of biological-state elements compared to solid-state devices, irrespective of the discovery of self-repair systems in photosynthetic microorganisms which prolong the lifetime of microbial proteins. This system involves a recycling process, in which damaged proteins are detected and destroyed [95].

The energy production efficiency is a major factor to consider in the comparison between PMFCs and solar panels. It was concluded that the use of PMFCs or phototrophic biofilms might be an alternative to photovoltaic solar panels to create energy-producing landscapes [96]. When applied in a natural environment, PMFC power yield is roughly estimated to be a maximum of 1.6 MW/km^2 [97], while solar panels could generate 4.5–7.5 MW/km^2 under Western European conditions (solar radiation 150 W/m^2 and power conversion efficiency; PCE 15–25%), [98] which means that the power output of solar panels will be three-to fivefold higher than that of PMFCs. However, the environmental impacts of solar panels, i.e. loss of green space and biodiversity, use of polluting metals, visual impact, increasing dark surface, are outsized leading to a wide societal argument [98,99]. PMFCs could offer an opportunity for electricity generation while sustaining the natural environment at locations where solar panels are not desirable. Future integration of PMFCs into closed systems could provide 24 h/day electricity generation without the use of scarce materials and with nutrient preservation.

7. Conclusions

Despite the power generated by abiotic cathodes of MFCs might look comparable with algal-based cathodes, but in the long term it is unsustainable and limited. Biotic algal-based systems require no replacement and provide sustained operation. The positive effect of illumination on microalgal cathodes proved the capability of phototrophic organisms to become operative biocatalysts by carrying out the role of active oxygenators, with the ability to produce electrical power under light and dark conditions. The microalgal photosynthetic biofilm appears to be an economic biocatalyst which is effective for the real world application of PMFCs as sustainable energy generators. Moreover, the technology of PMFC offers golden opportunities of enabling energy production along with the added value of carbon fixation from intractable waste materials and algal biomass production.

On the other hand, more studies are still required to scale up and optimize the integrated PMFC systems. This includes the creation of more effective coupled system design, taking into account the effect of PBR's and MFC's hydraulic retention time (HRT) on the growth of microalgae and their ability to remove pollutants. The overall recovered energy from the PMFC could be magnified by increasing the electrode surface area, which positively results in enriched biofilm and overcomes the competition of non-electrochemically active microorganisms.

There have been a breakthrough in molecular biology in the last decades, hence the genomes of several microorganisms have been sequenced. So upcoming studies should focus further on the genomic analyses in order to clarify physiological and genetic interactions and to provide the deep understanding of molecular mechanisms that motivate microbial interactions and related functions.

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